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LIQUID TONERS WITH ZIRCONIUM/ALUMINUM COMPLEX CHARGE
DIRECTOR

Abstract:

Abstract of WO9704363

The present invention provides a novel charge director which is a high molecular weight viscous complex of an aluminum soap and a zirconium soap. This Zirconium/Aluminum complex associates closely with toner particles and displays very little migration into toner carrier liquid. Data supplied from the esp@cenet database - Worldwide

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(54) Title: LIQUID TONERS WITH ZIRCONIUM/ALUMINUM COMPLEX CHARGE DIRECTOR (57) Abstract The present invention provides a novel charge director which is a high molecular weight viscous complex of an aluminum soap and a zirconium soap. This Zirconium/Aluminum complex associates closely with toner particles and displays very little migration into toner carrier liquid.		

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LIQUID TONERS WITH ZIRCONIUM/ALUMINUM COMPLEX CHARGE DIRECTOR

BACKGROUND OF THE INVENTION

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Field of Invention

This invention relates liquid toners useful in electrophotography. The invention relates especially to charge directors used in liquid toners.

10 Background of the Invention

In electrography and electrophotography a toner is deposited on a charged surface, typically an imagewise charged surface. Electrography generally comprises placing a charge onto selected areas of a dielectric medium with an electrostatic writing stylus or its equivalent to form a charge image, applying toner to the charge
15 image, and fixing the toned image.

Electrophotography forms the technical basis for various well known imaging processes, including photocopying and laser printing. A general discussion of color electrophotography is presented in "Electrophotography," by R. M. Schaffert, Focal Press, London & New York, 1975, pp. 178-190. The basic
20 electrophotographic process involves placing a uniform electrostatic charge on a photoreceptor element, imagewise exposing the photoreceptor element to light thereby dissipating the charge in the exposed areas, developing the resulting electrostatic latent image with a toner, and transferring the toner image from the photoreceptor element to a final substrate, such as paper, either by direct transfer
25 or via an intermediate transfer material.

In either electrography or electrophotography the process of forming a charge image and applying toner to that image may be repeated to give an image having one color superimposed upon another. U.S. Pat. No. 2,907,674 recommends the use of liquid toners for superimposed color images as opposed to
30 the earlier-discovered dry toners. Liquid toners typically comprise toner particles, which usually comprise a polymeric binder and either a pigment or a dye, dispersed

in a high resistivity carrier liquid, e.g., 10^9 ohm.cm or more. The liquid toners preferably further include an additive (referred to in this document as a "charge director") for enhancing the charge carried by the toner particles. Each pigment or dye possesses different charge characteristics and the charge directors may function to bring about greater uniformity in the charge characteristics of the toner particles. These charge directors frequently may also serve to stabilize the dispersion of the toner particles in the carrier liquid. The charge directors associate with the colorant particles by some mechanism, such as complexing, covalent or ionic bonding, adsorption on the surface of the particles, etc.

A variety of materials can be used as charge directors. Illustrative of known charge directors would be the polyoxyethylated alkyl surfactants such as polyoxyethylated alkylamine, polyoxyethylene palmitate, polyoxyethylene stearate, etc. Other useful materials are magnesium and heavier metal soaps of fatty and aromatic acids as described in Beyer, U.S. Pat. No. 3,417,019. See also U.S. Pat. Nos. 3,900,412; 3,417,019; 3,779,924; and 3,788,995. Useful metal soaps include cobalt naphthenate, magnesium naphthenate and manganese naphthenate, zinc resinate, calcium naphthenate, zinc linoleate, aluminum resinate, isopropyltitanium stearate, aluminum stearate, and others, many of which are also described in U.S. Pat. No. 3,259,581. Typically, the amount of such materials used is less than about 2 percent by weight based on the weight of toner. In certain instances, the resinous binder per se can function as the charge control agents, as can the colorant.

Unfortunately many known charge directors migrate from the toner particles into the carrier liquid. Such migration causes a deterioration in the image density and resolution. A variety of cures for this problem have been offered (See e.g., U.S. Pat. Nos. 3,900,413; 3,954,640; 3,977,983; 4,081,391; and 4,264,699). British Pat. 2,023,860 discloses centrifuging the toner particles out of a liquid toner and redispersing them in fresh liquid as a way of reducing conductivity in the liquid itself.

U.S. Pat. Nos. 4,547,449 and 4,606,989 advance the idea that the level of free charge within the liquid toner as a function of the mass of toner particles is important to the efficiency of the developing process. In U.S. Pat. No. 4,525,446,

the aging of the toner was measured by the charge present and related it generally to the zeta potential of the individual particles. A related patent, U.S. Pat. No. 4,564,574, disclosed that charge directing salts were chelated onto the polymer binder by specially incorporated moieties on the polymer. It further disclosed
5 measured values of zeta potential on toner particles. Zeta potential values of 33 mV and 26.2 mV and particle diameters of 250 nm and 400 nm were reported. The objective of that patent was to improve stability of the liquid toner. Attachment of the charge directing salts directly to the polymer chain necessitated the presence of the charge in a random orientation off of the polymer. The charge
10 would be generally distributed throughout the bulk and surface of the polymer. U.S. Pat. No. 4,155,862 disclosed that the charge per unit mass of the toner was related to difficulties experienced in the earlier art in superposing several layers of different colored toners. This latter problem was addressed in U.S. Pat. No. 4,275,136, wherein adhesion of one toner layer to another was enhanced by an
15 aluminum or zinc hydroxide additive on the surface of the toner particles.

U.S. Pat. 4,925,766 and 4, 978,598 used polymers having groups capable of forming covalent links with the metal soaps to reduce the amount of free charge directors in the carrier liquid.

One negative effect caused by the migration of the charge director from the
20 toner particles into the carrier liquid is that toner replenishers, which are more concentrated dispersions of toner particles in carrier liquid than are toner starter dispersions, must have a different formulation with regard to the amount of charge director than do toner starter dispersions.

25 SUMMARY OF THE INVENTION

The present invention provides a novel charge director which is a high molecular weight viscous complex of an aluminum soap and a zirconium soap. The aluminum soap, if used alone, is insoluble in the carrier liquid. However, when the aluminum soap is complexed with a zirconium soap, the resulting complex is fully
30 soluble in aliphatic hydrocarbon liquids, which are frequently used as carrier liquids.

This Zirconium/Aluminum complex associates closely with toner particles and displays very little migration into the carrier liquid.

A first embodiment this invention is a charge director which comprises a complex of a zirconium soap and an aluminum soap. This charge director complex has a viscosity of 10-200 cP, preferably 50-100 cP, more preferable 70-90 cP, at a total % solids of 10-15% in a hydrocarbon carrier liquid as measured on a Brookfield Digital Viscometer. The charge director complex may be formed by combining aluminum and zirconium soaps in a nonpolar solvent and heating gradually while stirring.

According to a second embodiment, this invention is a liquid toner comprising a dispersion of toner particles with associated Aluminum/Zirconium complex charge director in a carrier liquid. These liquid toners can be used as either toner starter dispersions or toner replenisher solutions because of the very low migration of charge director into the carrier liquid.

DETAILED DESCRIPTION OF THE INVENTION

The Aluminum/Zirconium charge director complex of this invention is the reaction product of an aluminum soap which is insoluble in a nonpolar solvent and a zirconium soap. Aluminum soaps useful in this invention may be represented by the general formula $Al^{+3}(OOCR)_nX_{3-n}^-$, wherein n is an integer from 1 to 3, preferably 2 or 3, most preferably 3; R is an alkyl group, an alkylene group, or an arylalkyl group of 2 to 30 carbon atoms, preferably 4 to 20 carbon atoms, and X is a monovalent anion. Examples of such aluminum soaps include, but are not limited to, aluminum palmitates, aluminum stearates, aluminum oleates, aluminum laurates, aluminum octanoates, aluminum hexanoates (e.g. 2-ethyl hexanoate), aluminum decanoates, etc. Aluminum stearates are preferred. As nonlimiting examples of X are OH⁻, Cl⁻, Br⁻, I⁻, and OR⁻, where R is as defined above. Hydroxy (OH⁻) is the preferred monovalent anion, X.

The zirconium soaps useful for the formation of the Aluminum/Zirconium charge director complex may be represented by the following formula:

$Zr(OOCR)_mY_{4-m}^-$, wherein m is an integer from 1 to 4, preferably 3 to 4, most

preferably 4; R' is an alkyl group, an alkylene group, or an arylalkyl group of 2 to 30 carbon atoms, preferably 4 to 20 carbon atoms, and Y is a monovalent anion. As nonlimiting examples of Y⁻ are OH⁻, OH⁻, Cl⁻, Br⁻, I⁻, and OR⁻, where R' is as defined above. Hydroxy (OH⁻) is the preferred monovalent anion, Y⁻. Since these
5 zirconium soaps are very sensitive to moisture, they may alternatively be found in the zirconyl soap state which is represented by the formula: (OOCR')₂. Examples of such zirconium soaps include, but are not limited to, zirconium palmitates, zirconium stearates, zirconium oleates, zirconium laurates, zirconium octanoates, zirconium hexanoates (e.g. 2-ethyl hexanoate), zirconium decanoates, etc.

10 As is well known to one skilled in the art, many of the above described soaps are frequently found in associated states which have complex structures that are not easily definable. See e.g., *Light-scattering Studies on Aluminum Distearate*, Leger, Hyde, and Sheffer, Canadian J. of Chem., vol. 36, 1958, pp. 1584-1595; *Colloidal Behavior of Cobalt Monooleate Soap in Apolar Organic Solvents*, Zhou et al., J. of Colloid and Interface Science, vol. 116, no. 2, April
15 1987, pp. 473-484. Thus, the above formulas are not intended to be limiting in regards to the structure in which such soaps are found under various conditions.

The charge director complex of this invention may be formed by combining the aluminum and zirconium soaps in a nonpolar solvent and heating gradually to
20 about 80 to 95 °C while stirring. The nonpolar solvent may be an aliphatic or an aromatic hydrocarbon. Examples of suitable aliphatic hydrocarbons include hexane, cyclohexane, iso-octane, heptane, and isododecane, and commercially available mixtures such as Isopars™ G, H, K, and L (from Exxon Corp.).

The complex is a highly viscous material which is soluble in the carrier
25 liquids commonly used in liquid toners. While not wishing to be bound to any theory, the Inventors believe that the Zr/Al complexes are structures that have metal-OH-metal type repeating units. In addition, the high viscosity of the complexes may indicate some cross-linking between organic chains.

The complex preferably has an zirconium/aluminum weight ratio in the
30 range of 5:1 to 100:1, more preferably 10:1 to 40:1.

The Aluminum/Zirconium charge director complex may advantageously be used in liquid toners which comprise a dispersion of toner particles in carrier liquid. The charge director complex associates with the toner particles and does not show significant migration into the carrier liquid. The toner particles comprise a colorant
5 in a resin or polymeric binder.

The carrier liquids used for the liquid toners of this invention may be any known carrier liquid. The carrier liquid is preferably chosen from non-polar liquids, more preferably hydrocarbons, which have a resistivity of at least 10^{11} ohm-cm and preferably at least 10^{13} ohm-cm, a dielectric constant less than 3.5 and a boiling
10 point in the range 140°C to 220°C. Aliphatic hydrocarbons such as hexane, cyclohexane, iso-octane, heptane, and isododecane, and commercially available mixtures such as Isopars™ G, H, K, and L (from Exxon Corp.) are suitable. However aromatic hydrocarbons, fluorocarbons, and silicone oils may also be used.

Dispersed in the carrier liquid are toner particles which comprise a
15 polymeric binder and a colorant. Any binder known for use in toner particles for liquid toners may be used. However, organosols (sometimes described as amphipathic particles) are preferred. Such organosols are complex molecules having at least one type of polymeric moiety which is solvated by the carrier liquid and at least one type of polymeric moiety which is non-solvated by the carrier
20 liquid. Such organosols are described in U.S. Pat. Nos. 3,753,760; 3,900,412, and 3,991,226. The binder systems disclosed in U.S. Pat. Nos. 4,925,766 and 4,988,602 are preferred.

As colorants, a wide range of pigments and dyes may be used. The only
25 criteria is that they be insoluble in the carrier liquid and be capable of being dispersed to a particle size below about a micrometer in diameter.

Suitable pigments include any one of the many now known to the art in connection with liquid electrostatographic developers. As is well known, these pigments essentially constitute very fine solid particles having a size in the submicron range and which are opaque en masse. They are insoluble in the liquid
30 system. Any pigments known in the art for use in toners may be used in the toner particles of this invention. Such pigments include but are not limited to

phthalocyanines, such as copper phthalocyanine; carbon black; nigrosine dye; Aniline Blue; Chrome Yellow; Dupont Oil Red (from DuPont); Monoline Yellow; Sunfast Blue, Sun Yellow, Sun Red and other pigments available from Sun Chemical Co.; Harmon Quindo Red; Regal 300; Fluorol Yellow 088, Fluorol Green Gold 084, Lumogen Yellow S 0790, Ultramarine Blue, Ultramarine Violet, Ferric Ferrocyanide, and other pigments available from BASF; Malachite Green Oxalate; lamp black; Rose Bengal; Malastral Red; magnetic pigments such as magnetite, ferrites, such as barium ferrite and manganese ferrite, hematite, etc. Preferably the pigments are not reactive with the polymeric binder.

10 If dyes are used as colorants they may be incorporated into the polymeric binder as a moiety of the organosol molecule or may be a separate molecule which is incorporated into the toner particle by second order or surface adsorption forces. Exemplary of the many suitable dyes held to the toner particle by second order or surface adsorption forces are C.I. Disperse Orange 26, C.I. Disperse Yellow 57, 15 C.I. Disperse Blue 77, C.I. Disperse Blue 73, C.I. Disperse Brown 2, C.I. Violet 27, C.I. Basic Blue 35, C.I. Basic Violet 15, C.I. Basic Red 26, C.I. Basic Blue 38, C.I. Basic Orange 30, C.I. Basic Red 24. Exemplary of the many suitable dyes which may bond to the polymeric binder and form chromophoric moieties are C.I. Acid Blue 7, C.I. Acid Blue 104, C.I. Acid Brown 14, C.I. Acid Yellow 63, C.I. 20 Black 26A, C.I. Solvent Red 41, C.I. Solvent Violet 9, C.I. Solvent Brown 12, C.I. Solvent Blue 4, C.I. Solvent Blue 6, C.I. Solvent Blue 2, C.I. Solvent Yellow 34, C.I. Solvent Green 1, and C.I. Solvent Red 49.

The liquid toners of this invention preferably have conductivities in the range of 5 to 500 pmho/cm. Preferably, at least 40%, and more preferably at least 80%, 25 of the charge is situated on the toner particles. The charge director complex of this invention is highly effective in keeping the charge associated with the toner particles and preventing migration of the charge into the carrier liquid. In fact, the charge director complex of this invention is so effective, that there is no need for distinct formulations for starter and replenisher toner solutions.

30 The invention is further illustrated by the following Examples.

EXAMPLES

Preparation of Aluminum/Zirconium Charge Director Complex:

Example 1

A mixture of 90 g of Zirconium Nuxtra 12 (zirconium 2-ethylhexanoate, 12% Zr from Huls America Inc.), 10 g of Aluminum tristearate, and 262.5 g of Isopar G™ was heated gradually to 95°C while stirring. When the temperature reached 70°C the Aluminum tristearate, which alone is insoluble in Isopar™ G, began to dissolve and the viscosity of the reaction mixture increased. The temperature was held at 95°C for about one hour until a homogeneous solution was attained. The solution was then cooled to room temperature. The resulting product did not exhibit any color and appeared clear. The resulting charge director complex had an Zirconium/Aluminum weight ratio of 23.3:1.

Example 2

The process of example 1 was repeated but this time 85 g of Zirconium Nuxtra and 15 g of Aluminum tristearate were used. The resulting product had a weight ratio of Zirconium to Aluminum of 37.2:1.

Example 3

The process of example 1 was repeated but this time 75 g of Zirconium Nuxtra and 25 g of Aluminum tristearate were used. The resulting product had a weight ratio of Zirconium to Aluminum of 12.4:1.

Preparation of Liquid Toners: Comparative Examples 4-6 and Examples 7-10

A charge director; an organosol polymeric binder as disclosed in U.S. Pat. 4,946,753, col. 17, line 36-42; Isopar-G™; a pigment; and, optionally a monovalent carboxylate soap were added to a clean container and mixed well. The mixture was placed in a sand mill and charged with 20-30 mesh sand. The mill was run for 0.5 to 3 hours.

Comparative Example 4

Comparative Example 4 was prepared from the following:

	Organosol* at 15.2% solids in Isopar™ G	2,004.72 g
	Isopar G	1,085.58 g
5	Sodium Stearate**	0.921 g
	Zirconium Ten Cem (Zr soap, Mooney Chemicals Co.)	32.6 g
	Regal 300 Carbon Black Pigment	76.18g

* Has 0.69 weight % hydroxy quinoline chelate based on weight solids

10 ** Sodium stearate was dissolved in the Zr soap before mixing with the organosol.

This toner had weight ratios (solids/solids) of:

	Organosol:pigment	4:1
	charge director:organosol	0.0506:1
15	Sodium stearate:charge director	0.0275:1

Comparative Example 5

Comparative Example 5 was prepared from the following:

	Organosol*at 15.46% solids in Isopar G	151.66 g
20	Isopar G	96 g
	Zirconium Nuxtra (Zr soap, Huls America Inc., 12%Zr)	6.47 g
	Regal 300 Carbon Black Pigment	5.86 g

* With 0.65 weight % hydroxy quinoline chelate based on weight solids

25 This toner had weight ratios (solids/solids) of:

	Organosol:pigment	4:1
	charge director:organosol	0.125:1

Comparative Example 6

30 Comparative Example 6 was prepared from the following:

	Organosol*at 15.46% solids in Isopar G	156.61 g
	Isopar G	93 g
	Zirconium Nuxtra (Zr soap Huls America Inc., 12% Zr)	4.36 g
	Sun Red 234-0077	3.63 g
35	Harmon RV-6803 Quindo	2.42 g

* With 0.65 weight % hydroxy quinoline chelate based on weight solids

This toner had weight ratios (solids/solids) of:

Organosol:pigment	4:1
charge director:organosol	0.075:1

5 Example 7

Example 7 was prepared from the following:

Organosol* at 15.2% solids in Isopar G	1933.72 g
Isopar G	1955 g
Charge Director complex from Example 1 (12% solids)	237.8 g
Regal 300 Carbon Black Pigment	73.8 g

* With 0.69 weight % hydroxy quinoline chelate based on weight solids

This sample had weight ratios (solids/solids) of:

Organosol:pigment	4:1
Charge director:organosol	0.1:1

This toner was used as a starter and a replenisher for imaging on a 3M Digital Matchprint™ Proofer. The starter developer concentration was adjusted to 0.4% solids and the replenisher concentration was at 12% solids. The starter developer was cycled to produce 100 images while replenishing at a rate of 1.2 grams/image. The quality of the image obtained from the first cycle was comparable to the quality of the image of the last cycle. The cycled developer maintained its charge per transmission optical density and conductivity throughout 100 cycles.

Example 8

Example 8 was prepared from the following:

Organosol* at 15.46% solids in Isopar G	151.66 g
Isopar G	56.4 g
Charge Director complex from Example 2 (6.36% solids)	46.08 g
Regal 300 Carbon Black Pigment	5.86 g

* With 0.65 weight % hydroxy quinoline chelate based on weight solids

This toner had weight ratios (solids/solids) of:

Organosol:pigment	4:1
Charge director:organosol	0.125:1

Example 9

Example 9 was prepared from the following:

5	Organosol* at 15.46% solids in Isopar G	155.63 g
	Isopar G	72.24 g
	Charge Director complex from Example 3 (10% solids)	22.12 g
	Regal 300 Carbon Black Pigment	6.01 g

* With 0.65 weight % hydroxy quinoline chelate based on weight solids

10

This toner had weight ratios (solids/solids) of:

15	Organosol:pigment	4:1
	Charge director:organosol	0.09:1

Example 10

Example 10 was prepared from the following:

20	Organosol* at 15.46% solids in Isopar G	154.59 g
	Isopar G	70.4 g
	Charge Director complex from Example 2 (6.3% solids)	28.45 g
	Sun Red 234-0077	3.63 g
	Harmon RV-6803 Quindo	2.42 g

* With 0.65 weight % hydroxy quinoline chelate based on weight solids

25

This toner had weight ratios (solids/solids) of:

30	Organosol:pigment	3.65:1
	Charge director:organosol	0.075:1

Example 11: Testing of the Liquid Toners

The Liquid toners prepared above were tested using a Keithley Digital Electrometer Model 616 and a TREK Power Supply Model 601 A-2 hooked to parallel conductive plates (PCP). The liquid toner was poured into a beaker containing the PCP so that toner is between the PCP. One of the conductive plates was transparent and attached to the negative electrode, the other was attached to the positive electrode. The toner was allowed to deposit for one second under about 1000 V/0.2 cm onto the transparent plate. The plate was dried and the transmission optical density was measured using a Gretag 182 Transmission

Densitometer. The charge was determined from the integrated i (current) vs t (time) curve. The conductivity was determined from the extrapolated current at 0 seconds time.

Particle size was measured with a Coulter N4MD Particle Size Analyzer.

- 5 The toners were used to form images in a Digital Matchprint Color Proofer (Minnesota Mining and Manufacturing Co.) and the image quality and tailing artifact were determined. The results are shown in the following Table.

TABLE OF RESULTS

Liquid Toner	Conductivity (pmho/cm)	Charge/TOD	TOD (1 sec rating)	Tailing artifact	Particle size (nm)
Comparative Example 4	99	0.1407	1.22	very significant	438
Example 7	78.4	0.0968	1.75	none	364
Comparative Example 5	111	0.1601	1.25	very significant	377
Example 8	70	0.1286	1.52	none	407
Example 9	60.7	0.1302	1.4	slight	384
Comparative Example 6	55.3	0.2143	0.82	significant	533
Example 10	53.1	0.1588	1.02	none	455

10

The toners having the inventive charge directors show higher transmission optical density than do toners having commercial charge directors. Images formed with toners having the inventive charge director also were substantially free of tailing artifacts and had high resolution of fine details.

What is claimed is:

1. A charge director comprising a complex of
an aluminum soap which is insoluble in hydrocarbon solvent and has
the formula $Al^{+3}(OOCR)_nX_{3-n}^-$, wherein n is an integer from 1 to 3, preferably 2 or
5 3, most preferably 3; R is an alkyl group, an alkylene group, or an arylalkyl group of
2 to 30 carbon atoms, preferably 4 to 20 carbon atoms, and X is a monovalent
anion, and
a zirconium soap represented by the formula $Zr(OOCR')_mY_{4-m}$,
wherein m is an integer from 1 to 4, preferably 3 to 4, most preferably 4; R' is an
10 alkyl group, an alkylene group, or an arylalkyl group of 2 to 30 carbon atoms,
preferably 4 to 20 carbon atoms, and Y is a monovalent anion.
2. The charge director of claim 1 wherein the aluminum soap is
selected from the group consisting of aluminum palmitates, aluminum stearates,
15 aluminum oleates, aluminum laurates, aluminum octanoates, aluminum hexanoates,
and aluminum decanoates.
3. The charge director of claim 1 wherein the zirconium soap is
selected from the group consisting of zirconium palmitates, zirconium stearates,
20 zirconium oleates, zirconium laurates, zirconium octanoates, zirconium hexanoates,
and zirconium decanoates.
4. The charge director of claim 1 having a viscosity of 10 to 200
centipoise at 10-15% solids.
25
5. The charge director of claim 1 wherein the complex is formed by
mixing, in a non-polar hydrocarbon solvent, the aluminum soap,
which is insoluble in non-polar hydrocarbon solvents and the zirconium soap
heating the mixture slowly to 80-95° C with continuous agitation
30 until a homogeneous mixture is formed.

6. A charge director comprising a complex of an aluminum soap and a zirconium soap wherein the complex is formed by
mixing, in a non-polar hydrocarbon solvent, the aluminum soap,
which is insoluble in non-polar hydrocarbon solvents, and the zirconium soap
5 heating the mixture slowly to 80-95° C with continuous agitation
until a homogeneous mixture is formed.

7. A liquid toner comprising toner particles, having a colorant and an
polymeric binder, dispersed in a carrier liquid and the charge director of claim 1
10 associated with the toner particles.

8. The liquid toner of claim 7 wherein the aluminum soap is selected
from the group consisting of aluminum palmitates, aluminum stearates, aluminum
oleates, aluminum laurates, aluminum octanoates, aluminum hexanoates, and
15 aluminum decanoates.

9. The liquid toner of claim 7 wherein the zirconium soap is selected
from the group consisting of zirconium palmitates, zirconium stearates, zirconium
oleates, zirconium laurates, zirconium octanoates, zirconium hexanoates, and
20 zirconium decanoates.

10. The liquid toner of claim 7 wherein the charge director has a
viscosity of 10-200 centipoise at 10-15% solids.

25 11. The liquid toner of claim 7 wherein the complex is formed by
mixing, in a non-polar hydrocarbon solvent, the aluminum soap,
which is insoluble in non-polar hydrocarbon solvents and the zirconium soap
heating the mixture slowly to 80-95° C with continuous agitation
until a homogeneous mixture is formed.

30

12. A liquid toner comprising toner particles, having a colorant and an polymeric binder, dispersed in a carrier liquid and the charge director of claim 6 associated with the toner particles.

5 13. The liquid toner of claim 7 wherein at least 40% of the charge in the toner is associated with the toner particles.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/08372

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G03G 9/135

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G03G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS, JAPIO, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5306590 (THOMAS FELDER), 26 April 1994 (26.04.94), column 6, line 40 - line 45; column 8, line 24 - line 25; column 12, line 58 - line 67, column 13, line 28 - line 39; column 13, line 51 - line 54; column 15, line 17 - line 25 --	1-3,5-9
A	US, A, 5378574 (FRANCOISE M. WINNIK ET AL), 3 January 1995 (03.01.95), column 11, line 41 - line 53 --	1-13
A	US, A, 5364726 (IAN D. MORRISON ET AL), 15 November 1994 (15.11.94), column 19, line 20 - line 32 --	1-13

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/08372

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4988602 (SUSAN K. JONGEWAARD ET AL), 29 January 1991 (29.01.91), column 9, line 19 - line 23 -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

31/07/96

International application No.

PCT/US 96/08372

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	5306590	26/04/94	NONE		
US-A-	5378574	03/01/95	EP-A,B-	0355062	21/02/90
			JP-A-	2110172	23/04/90
			US-A-	4877451	31/10/89
US-A-	5364726	15/11/94	EP-A-	0455343	06/11/91
			JP-A-	6236078	23/08/94
			JP-A-	4336543	24/11/92
			US-A-	5395724	07/03/95
US-A-	4988602	29/01/91	AU-B-	641489	23/09/93
			AU-A-	7434491	24/10/91
			CA-A-	2040640	19/10/91
			EP-A-	0453278	23/10/91
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